Inorganica Chimica Acta, 34 (1979) L273–L275
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Resonance Raman Spectra of $[Ni(dmg)_2]$, $[Pd(dmg)_2]$ and $[Pt(dmg)_2]$ in the Solid State (dmgH = dimethylglyoxime)

YUZO NISHIDA

Department of Chemistry, Faculty of Science, Kyushu University 33, Fukuoka 812, Japan

MUNETERU KOZUKA and KAZUO NAKAMOTO

Todd Wehr Chemistry Building, Marquette University, Milwaukee, Wis. 53233, U.S.A.

Received February 27, 1979

The origin of the well-resolved band at 538 nm of solid $[Ni(dmg)_2]$ has been controversial [1–7]. Several workers [2, 3] associated it with the intermolecular Ni–Ni interaction while other workers [5–7] attributed it to an electronic transition within the single molecule. Recently, resonance Raman (RR) spectroscopy has proved to be very useful in assigning the electronic spectra of coordination compounds [8, 9]. In this communication, we wish to report the RR spectra and excitation profiles of $[Ni(dmg)_2]$, $[Pd(dmg)_2]$ and $[Pt(dmg)_2]$ in the solid state and to provide definitive evidence to support the single-molecule theory advanced by the previous workers [5–7].

The title compounds were prepared according to the methods described in [5]. The resonance Raman spectra were measured by using a Spex Model 1401 double monochromator. Detection was made with a cooled RCA C31034 A photo-multiplier tube with DC amplification. Excitations at 476.5, 488.0 and 514.5 nm were made by a Spectra-Physics Model 164 Argon-ion laser and those at 579.0 and 550.0 nm were made by a Spectra-Physics Model 365 CW dye-laser (Rhodamine 6G, sodium fluorescein) pumped by the above 4W Argon-ion laser. To compare relative intensity, the internal standard (K_2SO_4) was mixed homogeneously with the sample in a KBr pellet. All the intensities were corrected for the ν^4 dependence and detector response. The rotating sample technique was used to avoid thermal decomposition.

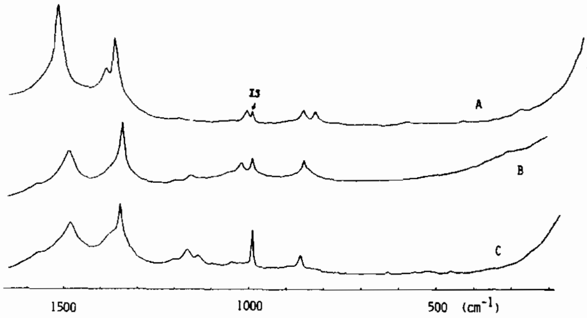
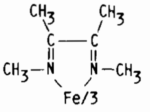
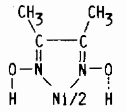


Fig. 1. The Raman spectra of the compounds. A: $[Ni(dmg)_2]$ (488.0 nm); B: $[Pd(dmg)_2]$ (476.5 nm); C: $[Pt(dmg)_2]$ (514.5 nm) (IS indicates the 980 cm^{-1} band of K_2SO_4 which was added as the internal standard).

Figure 1 shows the RR spectra of the three compounds obtained by using the exciting lines listed in the legend. It is seen that all the compounds exhibit similar spectra with two or three strong bands in the 1550–1300 cm^{-1} region (Table I). It was also noted that these spectra are strikingly similar to that of the $[Fe(bmi)_3]^{2+}$ ion in aqueous solution [10].



$[Fe(bmi)_3]^{2+}$



$[Ni(dmg)_2]$

At 514.5 nm excitation, for example, $[Fe(bmi)_3]^{2+}$ exhibits three bands at 1542 (strong), 1400 (medium) and 1334 cm^{-1} (strong) while $[Ni(dmg)_2]$ shows the corresponding bands at 1510 (strong), 1379 (medium) and 1355 cm^{-1} (strong) (see Fig. 2). Evidently these bands are due to the CN, CC stretching or their coupled vibrations of the α-diimine skeleton [10] which is common to both compounds.

Figure 2 shows the RR spectra of $[Ni(dmg)_2]$ as a function of the exciting frequency. The excitation profiles shown in Fig. 3 were obtained by plotting the relative intensities of the two strong α-diimine bands at 1510 and 1355 cm^{-1} as a function of the exciting frequency (the electronic spectra shown in Figs. 3–5 were taken from the work of Basu *et al.* [5]). It is seen that the intensities of these two bands are

TABLE I. Electronic Absorption Maxima and Resonance-enhanced Bands.

Complex	λ_{max}(nm) [7]	Resonance-enhanced Bands (cm^{-1})		
$[Ni(dmg)_2]$	538	1510,	1379,	1355
$[Pd(dmg)_2]$	465	1479,		1342
$[Pt(dmg)_2]$	662	1477,		1336

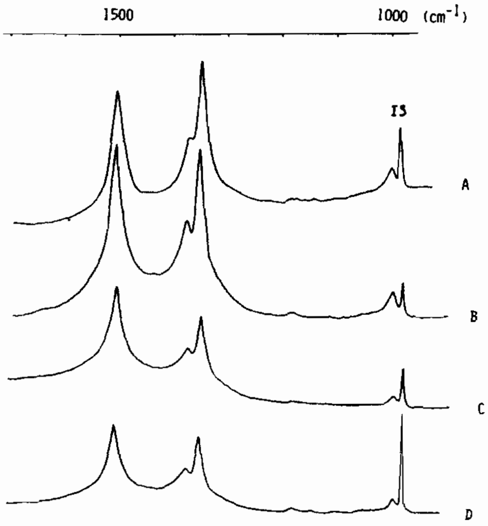


Fig. 2. The resonance Raman spectra of [Ni(dmg)$_2$]. A: 579.0 nm; B: 514.5 nm; C: 488.0 nm; D: 476.5 nm (IS indicates the 980 cm^{-1} band of K_2SO_4 which was added as the internal standard).

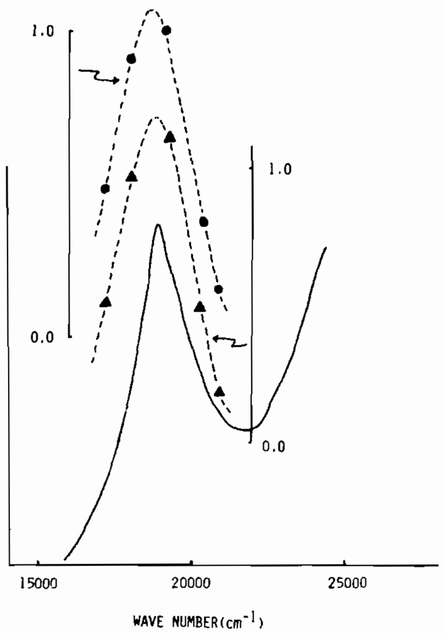


Fig. 3. The excitation profiles of [Ni(dmg)$_2$]. ▲ 1510 cm^{-1} band; ● 1355 cm^{-1} band.

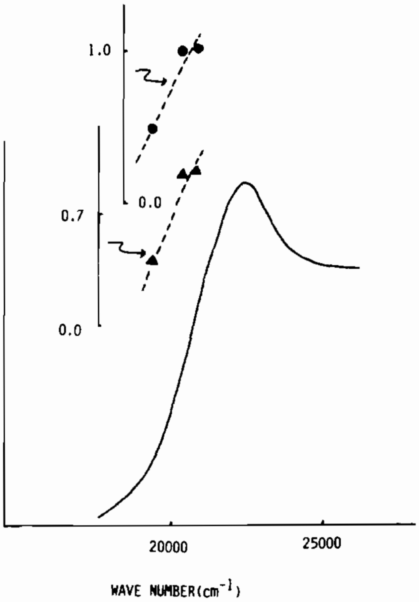


Fig. 4. The excitation profiles of [Pd(dmg)$_2$]. ▲ 1479 cm^{-1} band; ● 1342 cm^{-1} band.

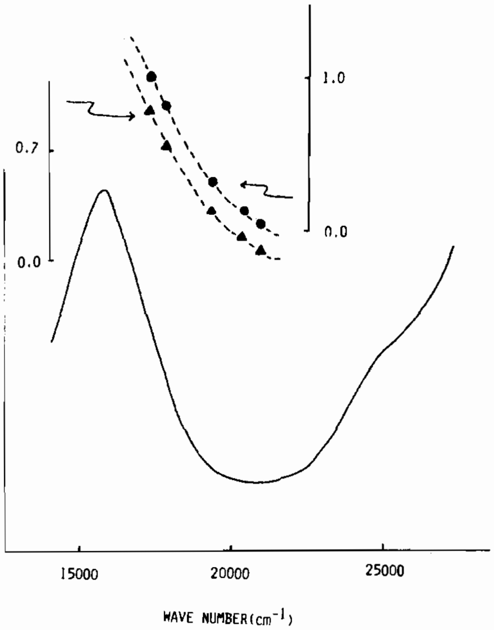


Fig. 5. The excitation profiles of [Pt(dmg)$_2$]. ▲ 1477 cm^{-1} band; ● 1336 cm^{-1} band.

maximized near the electronic absorption peak at 538 nm. This result definitely supports the previous workers [5–7] who attributed the 538 nm band to an electronic transition within a single molecule. The single-molecule theory is also supported by the fact that no strong resonance enhancement of the Ni–Ni stretching mode has been observed in the low frequency region.

Figures 4 and 5 show excitation profiles of [Pd(dmg)$_2$] and [Pt(dmg)$_2$], respectively. Unfortunately, these profiles are not complete due to the lack of proper exciting laser sources near the absorption maximum. It is reasonable, however, to expect similar results for these compounds since previous workers [5–7] have already demonstrated that the nature of the visible bands is the same for all three compounds. Finally, the nature of the intramolecular electronic transition involved in resonance enhancement is not immediately obvious from our work. In the case of the $[Fe(bmi)_3]^{2+}$ ion, the strong Fe → ligand CT transition at 568 nm was responsible for resonance enhancement. In general, strong resonance effect is observed only for electronic transitions accompanied with large oscillator strengths. In this respect, the present result seems to prefer the mixing of $3d_{z^2} \rightarrow 4p_z$ and a metal → ligand CT [6] rather than pure $3d_{z^2} \rightarrow 4p_z$ transition [7] as a possible origin of the visible bands of the title compounds.

Acknowledgements

The authors wish to thank Professor S. Kida of Kyushu University for his helpful discussions. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

References

1 T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev., 1,* 99 (1972).
2 S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Jpn., 27,* 156 (1954).
3 C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc., 80,* 4767 (1958).
4 J. C. Zahner and H. G. Drickamer, *J. Chem. Phys., 33,* 1625 (1960).
5 G. Basu, G. M. Cook and R. L. Belford, *Inorg. Chem., 3,* 1361 (1964).
6 B. G. Anex and F. K. Krist, *J. Am. Chem. Soc., 89,* 6114 (1967).
7 Y. Ohashi, I. Hanazaki and S. Nagakura, *Inorg. Chem., 9,* 2551 (1970).
8 T. G. Spiro, *Acc. Chem. Res., 7,* 339 (1974).
9 D. P. Strommen and K. Nakamoto, *J. Chem. Educ., 54,* 474 (1977).
10 R. J. H. Clark, P. C. Turtle, D. P. Strommen, B. Streusand, J. Kincaid and K. Nakamoto, *Inorg. Chem., 16,* 84 (1977).